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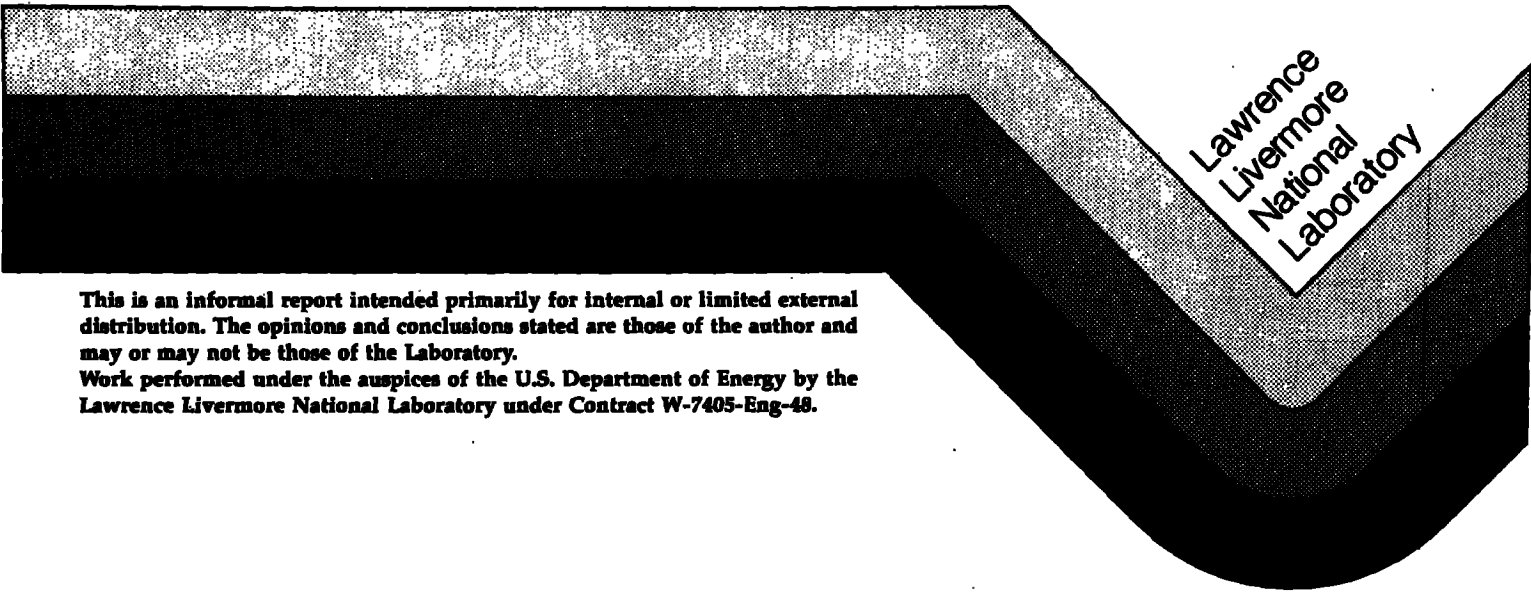
LAWRENCE LIVERMORE NATIONAL LABORATORY
OIL SHALE PROJECT QUARTERLY REPORT

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A. E. LEWIS EDITOR

For
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Laramie, Wyoming

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I. DETERMINATION OF INORGANIC NITROGEN IN SHALE

We have previously reported on two ways of estimating the inorganic nitrogen content of oil shale. One method is based on the assumption that the nitrogen left after shale is oxidized (by low-temperature ashing) is inorganic. The other method is based on the assumption that the org.N/org.C ratio in shale is constant as follows:

$$\text{Fraction inorg. N} = \frac{\text{Wt\%N} - 0.0276(\text{Wt\% org.C})}{\text{Wt\%N}}$$

Figure 1 shows a comparison of the results for 11 shales by the two methods. A trend is clear but the correspondence is only qualitative.

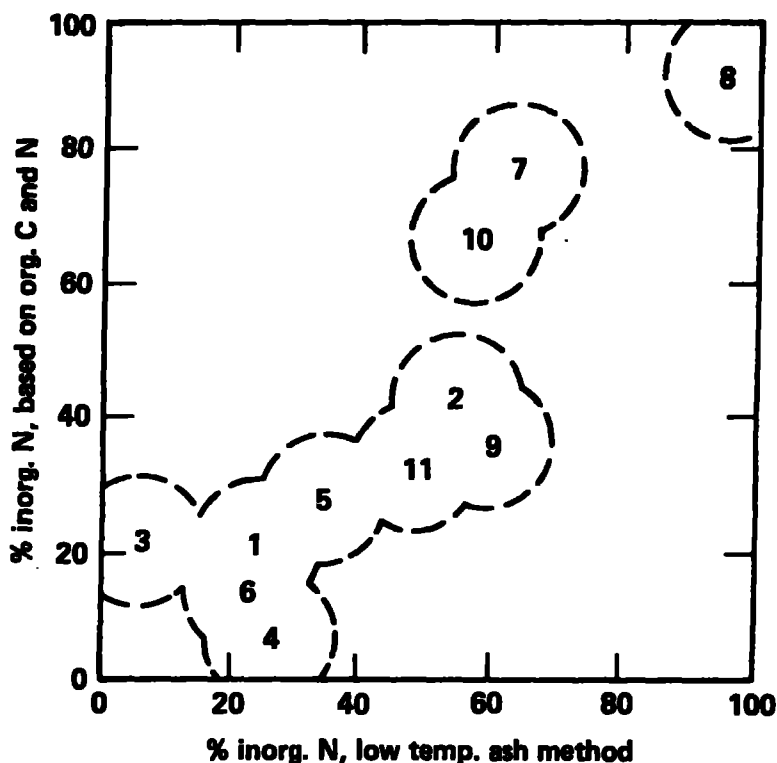


Fig. 1. Comparison of inorg. N content of 11 shale samples
as determined by two methods.

II. RETORT MODELING

Our moving-bed retort model was used to investigate the effects of shale flow rate, shale grade, and water content for a 50000 barrel/day plant using an external-combustion, hot-gas retort.

The effects of increasing the raw shale rate per unit retort by a factor of 3 are shown in Fig. 2. The total compressor power is seen to increase by a factor of 9 from 5 MW to 45 MW. That is, the compressor power goes up with the square of the shale rate. This is to be expected, because the required recycle gas rate is directly proportional to the raw shale rate; and the pressure drop, in turn, is proportional to the square of the recycle gas velocity, since the flow is in the turbulent regime. The number of unit retorts for a 50000 barrel/day plant, however, decreases only by a factor of 3, from 12 retorts to 4 retorts. The capital savings in retorts may be largely offset by the higher capital and operational expense for the much higher compressor power.

The effects of increasing the raw shale grade are, to a point, largely beneficial. Fig. 3 shows that, in going from 24 gal/ton to 36 gal/ton, the amount of oil that must be burned to heat the recycle gas decreases from 6.5% FA to only 1.3% FA. Likewise, the number of unit retorts drops from nearly 7.7 to 5. Our model calculations, however, do not account for attrition or compaction of the shale particles. At some point as a higher grade is used, the organic phase becomes the continuous phase in a shale particle. Then, upon pyrolysis of the kerogen, a very fine residue of inorganic material may cause loss of permeability in the retort and thus preclude satisfactory operation.

The water content of the shale has many interesting effects. The base-case water content is 1.5 wt%, and the corresponding total recycle gas flow rate of 17000 mol/s and 0.25 atm pressure drop are shown in Fig. 4. Of more interest, is the effect of much larger amounts of water, particularly from free water such as surface moisture or included water as found in both Israeli shale and Australian shale. Fig. 4 illustrates that if, instead of 1.5 wt% water, the total water content were 20 wt%, the recycle gas requirement would increase by a factor of 2.5 from 17000 mol/s to 42000 mol/s to supply the additional energy for water vaporization. The recycle gas increase is not linear with water content, because part of the energy for water vaporization is regained by condensation of some of the water lower in the retort. The pressure drop for the ten-fold increase in water content is seen to increase by a factor of 5.

What this means in a more economic sense is shown in Fig. 5. The compressor power, over this range of water content, increases by a factor of nearly 7 from 21 MW to over 140 MW. On the other hand, there is only a moderate 40% increase in the recycle heater load. This moderate increase in recycle heater load is due, in part, to the fact that the large increase in compressor power itself contributes significantly to the temperature rise of the recycle gas.

Despite the moderate increase in recycle heater load, the relative amount of oil that must be burned in the recycle heater increases appreciably, from 3.3% FA to 8% FA, as shown in Fig. 6. While this may seem like a dilemma at first glance, we must remember that for the base case, a large fraction of the recycle gas heater fuel consists of the product gas recovered in the process, whereas the incremental fuel over and above that is furnished by the product shale oil.

Finally, we also see in Fig. 6 that there is a large increase in the condenser heat load from 44 MW to over 400 MW, an increase that is essentially linear with water content of the raw shale. The bottom line as far as water content is concerned is that a retort is probably not the best way to dry shale, particularly if the water content is more than a few wt%. There would be other sources of low-grade heat that could be used more economically for this purpose than burning additional oil or other valuable fuel and causing the high pressure drop due to the high flow of gas through the retort.

III. REDUCED VOLUME SAMPLING SYSTEM INSTALLED ON TRIPLE QUADRUPOLE MASS SPECTROMETER

An online tripole quadrupole mass spectrometer (TQMS) is currently being used to monitor the concentration of H_2S and nine other trace level gaseous sulfur species during retort operation. In order to improve the ability of the instrument to monitor transient events a new reduced volume sampling system has recently been installed. Using the previous sampling system approximately 30 minutes were required to achieve a steady state signal upon the introduction of a new gas feed. The new sampling system has been found to have a characteristic sweep out time of less than 5 minutes. The ability of the system to monitor short duration events is demonstrated in Figure 7.

The transient events observed in the concentration of H_2S and COS in the pyrolysis gas were caused by stopping the recycle of burned shale supplied to the retort pyrolyzer. The reduction in H_2S concentration is

presumably caused by the drop in pyrolyzer temperature resulting from the absence of recycled shale which acts as the primary source of heat to the pyrolyzer. Note that the time corresponding to the minimum H_2S concentration corresponds to a maximum in COS concentration. This suggests that the reactions responsible for the production of H_2S and COS compete for a common source of sulfur.

IV. VISITORS

- | | |
|------------|--|
| 1/3/85 | Dr. Michael Silverman, Senior Research Chemist and Dr. Blaine Binger, Regulatory Affairs Management with Tenneco Oil Company, Texas. |
| 1/22-24/85 | Jer-Yu Shang, Deputy Director and Carl Roosmagi, DOE Morgantown Energy Technology Center, Morgantown, West Virginia. |
| 1/29/85 | Billy Joe Thorne and Thomas C. Bickel, Sandia National Laboratory, Albuquerque, New Mexico. |
| 3/21/85 | Billy Joe Thorne, Sandia Albuquerque, Albuquerque, New Mexico. |

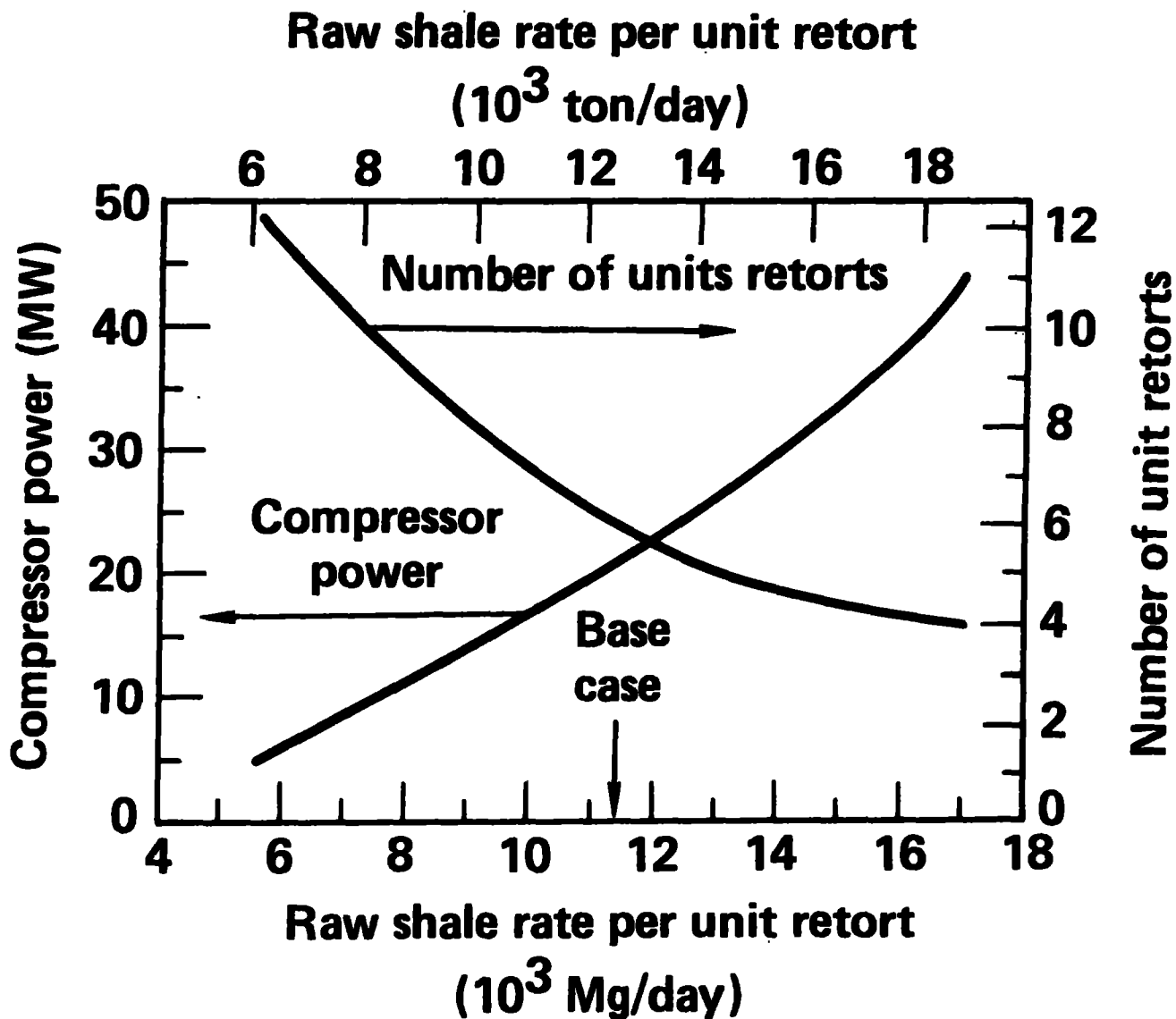


Figure 2. Effect of raw shale rate per unit retort on total compressor power and number of unit retorts required (30 gal/ton shale).

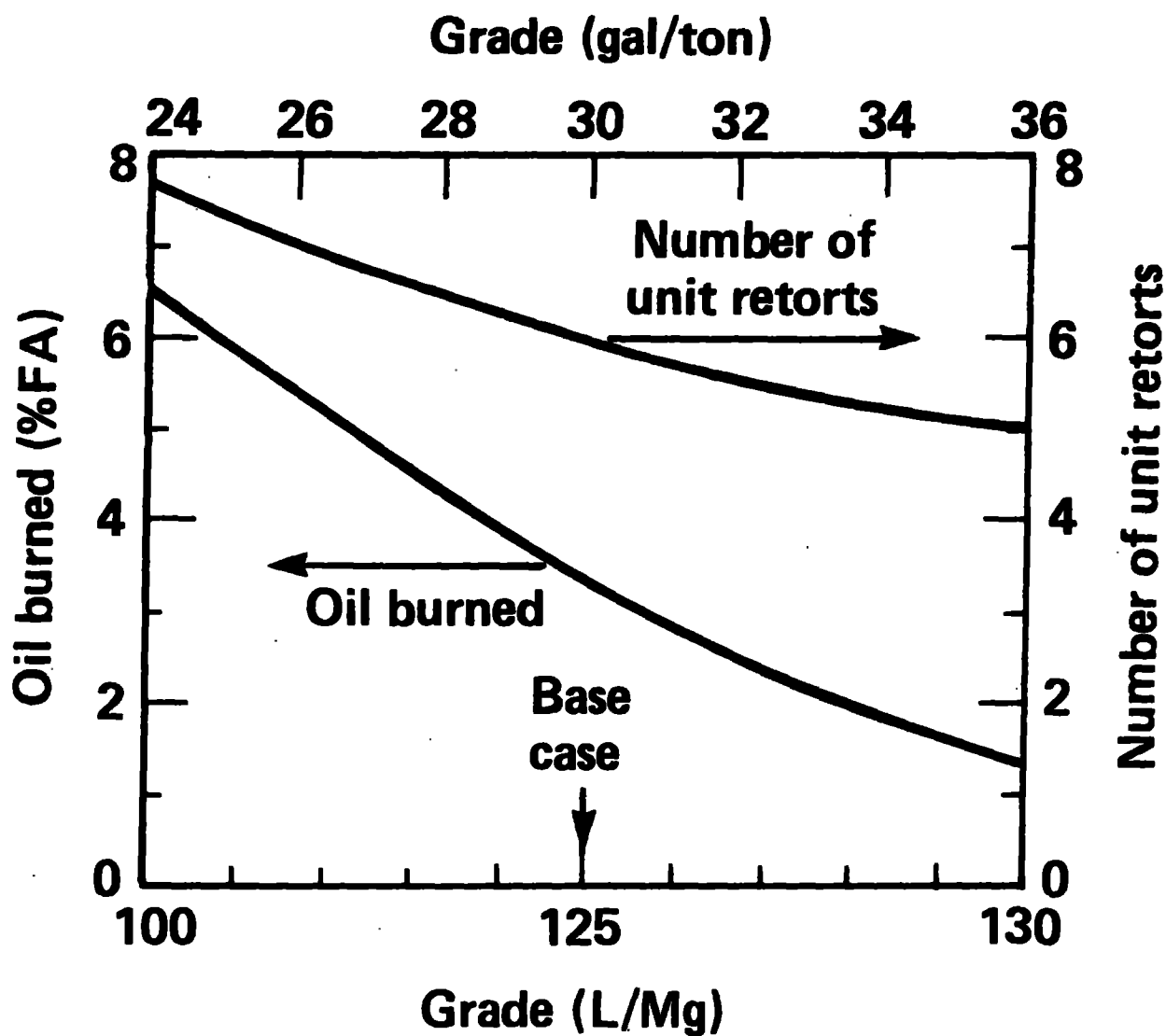


Figure 3. Effect of shale grade on amount of oil burned and number of unit retorts required.

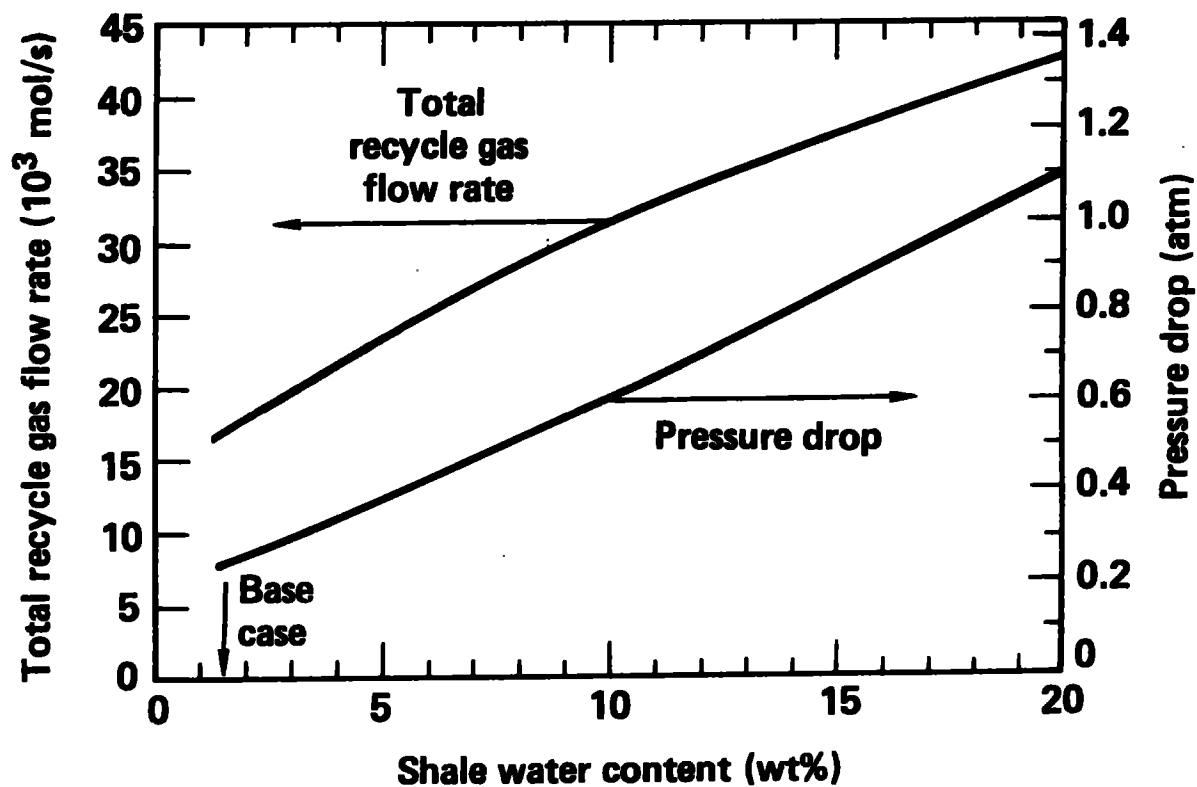


Figure 4. Effect of shale water content on total required recycle gas flow rate and retort pressure drop.

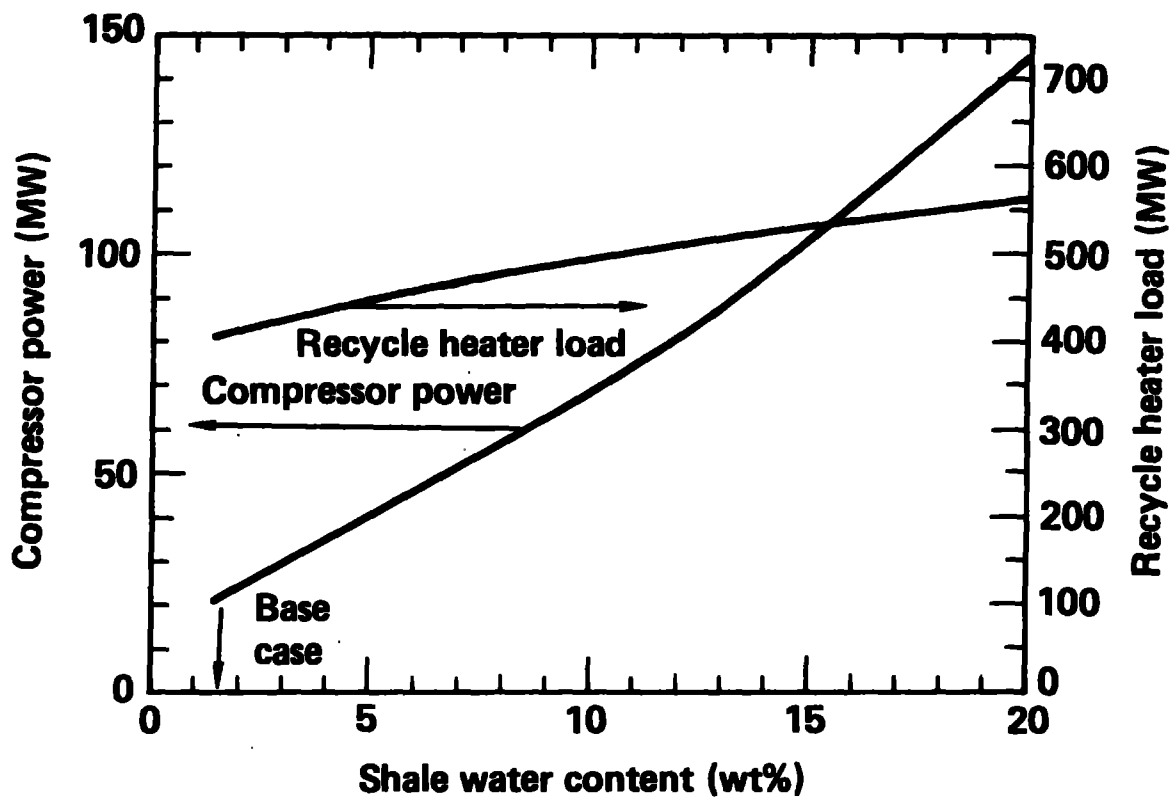


Figure 5. Effect of shale water content on compressor power and recycle heater load.

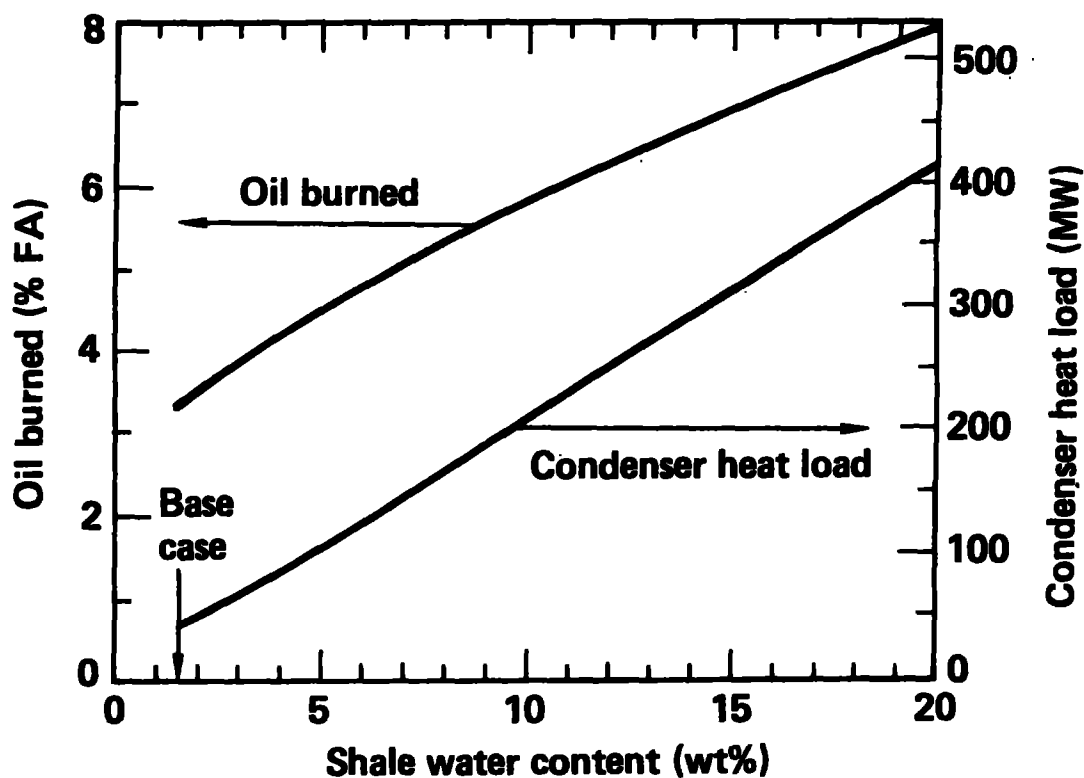


Figure 6. Effect of shale water content on required oil fuel and condenser heat load.

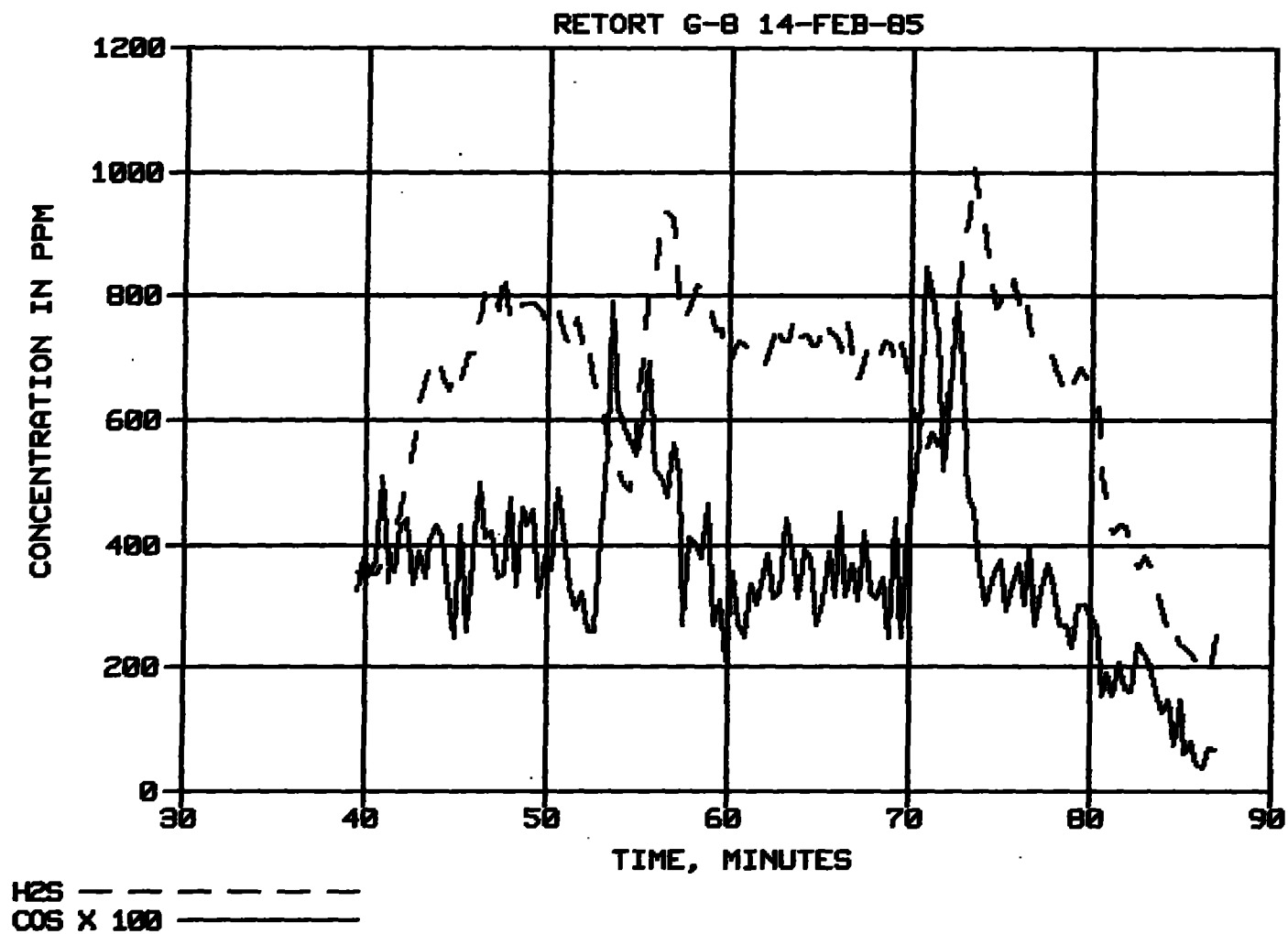


Figure 7.

V. PUBLICATIONS

- UCRL-92079 R. L. Braun and A. K. Burnham, "Kinetics of Colorado Oil Shale Pyrolysis in a Fluidized-Bed Reactor", submitted to Fuel.
- UCRL-91927 R. L. Braun and A. E. Lewis, "Results of Mathematical Modeling of Oil Shale Retorting in an Aboveground, External Combustion, Moving Bed Retort", 18th Annual Oil Shale Symposium, to be presented April 22-26, 1985, Colorado School of Mines, Golden, Colorado. (Submitted for publication in Fuel Processing Technology.)
- UCRL-90155 R. W. Taylor, C. J. Morris, and A. K. Burnham, "Nitric Oxide (NO) Emissions from Combustion of Retorted Oil Shale", 18th Annual Oil Shale Symposium, to be presented April 22-26, 1985, Colorado School of Mines, Golden, Colorado.